

## Synthesis, Crystal Structure and Fluorescence Spectrum of a Europium Compound $[\text{Eu}(\text{NO}_3)_3(\text{H}_2\text{O})_4] \cdot (\text{C}_{10}\text{H}_9\text{N}_2)_2 \cdot (\text{NO}_3)_2$

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A europium compound with the general molecular composition  $[\text{Eu}(\text{NO}_3)_3(\text{H}_2\text{O})_4] \cdot (\text{C}_{10}\text{H}_9\text{N}_2)_2 \cdot (\text{NO}_3)_2$  was synthesized from 4,4'-bipyridyl and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in ethanol and characterized by elemental analysis, molar conductance, IR, TG and X-ray crystallographically. The single-crystal X-ray diffraction studies demonstrated that compound is crystallize in triclinic system, space group  $P_1$ , with  $a = 0.8112(3)$  nm,  $b = 1.2797(3)$  nm,  $c = 1.5164(2)$  nm,  $\alpha = 95.158^\circ$ ,  $\beta = 101.732^\circ$ ,  $\gamma = 100.174^\circ$ ,  $V = 1.504(2)$  nm<sup>3</sup>,  $Z = 2$ ,  $M_r = 848.46$ ,  $F_{(000)} = 848.0$ ,  $D_c = 1.873$  g cm<sup>-3</sup>,  $\mu$  ( $M_0K\alpha$ ) = 1.056 mm<sup>-1</sup>. It turned out that three nitrate anions coordinate to Eu(III) as bidentate and four water molecules coordinate to Eu(III), forming a ten-coordination distorted dicapped square antiprism geometry. In addition, the luminescent property and fluorescence quenching interaction with EB-DNA have been studied. CCDC: 871243.

**Key Words:** Europium compound, 4,4'-Bipyridyl, Crystal structure, Luminescent property, EB-DNA.

### INTRODUCTION

Lanthanide complexes have grabbed some serious attention rapidly in function material field. Not only for the varieties of coordination model<sup>1,2</sup>, but also for their special chemical and physical characteristics arising from 4f electrons, such as fluorescent<sup>3-5</sup> and magnetism<sup>6,7</sup>. Taking advantage of the high affinity with oxygen, the high and variable coordination numbers, flexible coordination geometry of lanthanide ions, a number of lanthanide compounds with diverse dimensionality and topologies have been synthesized<sup>4,5</sup>. Most of which have narrow emission bands, high fluorescence efficiencies and excellent fluorescence monochromaticity, so they can be applied in a lots of areas such as organic electroluminescent devices, light conversion materials, optical microcavity emitters, etc.<sup>8,9</sup>. Among them, the  $\text{Eu}^{3+}$  compounds is one of the most important luminescent materials, their strong red, long-lived and line-like emissions have made them of widespread interest for a series of applications from biological assays to display devices<sup>10,11</sup>. In this paper a new  $\text{Eu}^{3+}$  compound was prepared and the optical properties were investigated in detail. As an extension of our work in this field, the DNA-binding property of the compound were investigated by spectrophotometric method. The experimental results suggest that the compound bind to DNA in an intercalation mode.

### EXPERIMENTAL

All reagents and solvents used were of commercially available quality and without purified before using. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4000-400 cm<sup>-1</sup>. Elemental analysis was performed on C, H, N elemental analyzer, Elementar Vario EL III. A Mettler Toledo thermal analyzer TGA/SDTA 851° was used to carry out the thermoanalytical analysis with a heating rate of 10 °C min<sup>-1</sup> from 30-800 °C in air atmosphere. Molar conductance was recorded on a DDS-11A conductivity meter at 25 °C. Fluorescent spectrum were recorded at room temperature on an Edinburgh FL920 phosphorimeter.

**Synthesis of the compound:** 4,4'-Bipyridyl (0.156 g, 1 mmol) was dosolved in ethanol (10 mL), then  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.485 g, 1 mmol) dissolved in water (10 mL) was added to the above solution with stirring for 3 h. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray work were obtained after two weeks. Yield: 46 % based on  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Anal. calcd. (%) for  $\text{C}_{20}\text{H}_{26}\text{N}_9\text{O}_{19}\text{Eu}$ : C, 28.33; H, 3.09; N, 14.86; Eu, 17.91. Found (%): C, 28.57; H, 3.21; N, 14.64; Eu, 17.73. IR (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3443 (w), 3054(w), 1540 (s), 1523 (s), 1503 (s), 1414(s), 1384 (s), 1360(m), 1305(s), 1210(m), 1078 (s), 1035(w), 815(w), 715(w).

**Fluorescence quenching experiments:** 2.0 mL EtBr solution ( $100 \mu\text{g mL}^{-1}$ ) and 1 mL DNA solution ( $200 \mu\text{g mL}^{-1}$ ) were added to 10 mL colorimetric tube, the DNA-binding ability of the compound to EB-DNA was studied in 2 mL *tris*-HCl/NaCl buffer (pH = 7.4). After standing for 2 h, gradually with adding a certain amount of the compound solutions to the mixture at 4 °C and reacting for 12 h. The excitement wavelength was aroused at 251 nm and each sample solution was scanned in the range 520-700 nm.

**X-Ray crystallography:** A single crystal of the compound with dimensions of 0.354 mm  $\times$  0.288 mm  $\times$  0.202 mm was selected and mounted on a glass fiber and collected diffraction

data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated  $\text{M}_0\text{K}_\alpha$  radiation ( $\lambda = 0.071073 \text{ nm}$ ) at 296(2) K. Structure was solved by direct methods using SHELXS-97<sup>12</sup> and refined on the  $F^2$  by full-matrix least-square method with SHELXL-97<sup>13</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined by using a riding mode. Experimental details for X-ray data collection are presented in Table-1 and the selected bond lengths and angles are listed in Table-2. CCDC No. 871243 of **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR THE COMPLEX

Empirical formula	$\text{C}_{20}\text{H}_{26}\text{N}_9\text{O}_{19}\text{Eu}$	Calculated density ( $\text{Mg/m}^3$ )	1.873
Formula weight	848.46	Absorption coefficient ( $\text{mm}^{-1}$ )	2.186
Temperature (K)	296(2)	$F_{(000)}$	848.0
Wavelength (nm)	0.071073	Crystal size (mm)	$0.354 \times 0.288 \times 0.202$
Crystal system	Triclinic	$\theta$ range for data collection ( $^\circ$ )	1.63 to 27.53
Space group	$P_1$	Limiting indices	$-10 \leq h \leq 10, -16 \leq k \leq 16, -19 \leq l \leq 19$
a (nm)	0.8112(3)	Reflections collected/unique	23896/6866 [ $R_{\text{int}} = 0.0225$ ]
b (nm)	1.2797(3)	Refinement method	Full-matrix least-squares on $F^2$
c (nm)	1.5164(2)	Data/restraints/parameters	6866/0/446
$\alpha$ ( $^\circ$ )	95.158(1)	Goodness-of-fit (on $F^2$ )	0.997
$\beta$ ( $^\circ$ )	101.732 (1)	Final R indices [ $I > 2\sigma(I)$ ]	$R_1=0.0189, wR_2 = 0.0485$
$\gamma$ ( $^\circ$ )	100.174(1)	R indices (all data)	$R_1 = 0.0211, wR_2 = 0.0498$
Volume ( $\text{nm}^3$ )	1.50417(2)	$\Delta\rho$ max, $\Delta\rho$ min ( $\text{e nm}^{-3}$ )	540 and -494
Z	2	–	–

TABLE 2  
SELECTED BOND LENGTHS (nm) AND ANGLES ( $^\circ$ )

Bond	Length	Bond	Length	Bond	Length
Eu(1)-O(1W)	0.24058(15)	Eu(1)-O(5)	0.24786(14)	Eu(1)-O(13)	0.25589(15)
Eu(1)-O(2W)	0.24070(14)	Eu(1)-O(12)	0.24967(14)	Eu(1)-O(8)	0.25900(15)
Eu(1)-O(3W)	0.24129(14)	Eu(1)-O(10)	0.25232(15)	Eu(1)-O(6)	0.28067(16)
Eu(1)-O(4W)	0.24607(14)	–	–	–	–
Angle	( $^\circ$ )	Angle	( $^\circ$ )	Angle	( $^\circ$ )
O(1W)-Eu(1)-O(2W)	78.47(6)	O(13)-Eu(1)-O(6)	104.52(5)	O(3W)-Eu(1)-O(8)	70.66(5)
O(1W)-Eu(1)-O(3W)	74.28(5)	O(8)-Eu(1)-O(6)	104.42(5)	O(4W)-Eu(1)-O(8)	67.16(5)
O(2W)-Eu(1)-O(3W)	71.79(5)	O(1W)-Eu(1)-N(6)	73.84(5)	O(5)-Eu(1)-O(8)	66.50(5)
O(1W)-Eu(1)-O(4W)	138.57(5)	O(2W)-Eu(1)-N(6)	96.79(5)	O(12)-Eu(1)-O(8)	149.73(5)
O(2W)-Eu(1)-O(4W)	131.88(5)	O(3W)-Eu(1)-N(6)	147.70(5)	O(5)-Eu(1)-N(7)	91.14(5)
O(3W)-Eu(1)-O(4W)	135.34(5)	O(4W)-Eu(1)-N(6)	74.87(5)	O(12)-Eu(1)-N(7)	133.41(5)
O(1W)-Eu(1)-O(5)	146.10(5)	O(5)-Eu(1)-N(6)	133.06(4)	O(10)-Eu(1)-N(7)	24.85(5)
O(2W)-Eu(1)-O(5)	78.00(5)	O(12)-Eu(1)-N(6)	25.21(5)	O(13)-Eu(1)-N(7)	84.61(5)
O(3W)-Eu(1)-O(5)	75.38(5)	O(10)-Eu(1)-N(6)	90.95(5)	O(8)-Eu(1)-N(7)	25.19(5)
O(4W)-Eu(1)-O(5)	75.01(5)	O(13)-Eu(1)-N(6)	24.84(5)	O(6)-Eu(1)-N(7)	122.11(5)
O(1W)-Eu(1)-O(12)	78.83(5)	O(8)-Eu(1)-N(6)	129.51(5)	N(6)-Eu(1)-N(7)	108.90(5)
O(2W)-Eu(1)-O(12)	73.48(5)	O(6)-Eu(1)-N(6)	86.91(5)	O(1W)-Eu(1)-H(1WA)	13.9
O(3W)-Eu(1)-O(12)	139.42(5)	O(1W)-Eu(1)-N(7)	98.67(5)	O(2W)-Eu(1)-H(1WA)	72.6
O(4W)-Eu(1)-O(12)	84.25(5)	O(3W)-Eu(1)-O(10)	86.95(5)	O(3W)-Eu(1)-H(1WA)	60.6
O(5)-Eu(1)-O(12)	116.81(5)	O(4W)-Eu(1)-O(10)	76.95(5)	O(4W)-Eu(1)-H(1WA)	150.5
O(1W)-Eu(1)-O(10)	77.12(6)	O(5)-Eu(1)-O(10)	115.96(5)	O(5)-Eu(1)-H(1WA)	132.6
O(2W)-Eu(1)-O(10)	151.17(6)	O(12)-Eu(1)-O(10)	116.03(5)	O(12)-Eu(1)-H(1WA)	89.4
O(10)-Eu(1)-O(8)	49.63(5)	O(1W)-Eu(1)-O(13)	71.68(5)	O(10)-Eu(1)-H(1WA)	80.1
O(13)-Eu(1)-O(8)	107.16(5)	O(2W)-Eu(1)-O(13)	119.43(5)	O(13)-Eu(1)-H(1WA)	85.4
O(1W)-Eu(1)-O(6)	138.85(5)	O(3W)-Eu(1)-O(13)	140.33(5)	O(8)-Eu(1)-H(1WA)	110.4
O(2W)-Eu(1)-O(6)	67.93(5)	O(4W)-Eu(1)-O(13)	68.48(5)	O(6)-Eu(1)-H(1WA)	139.0
O(3W)-Eu(1)-O(6)	114.47(5)	O(5)-Eu(1)-O(13)	141.90(5)	N(6)-Eu(1)-H(1WA)	87.2
O(4W)-Eu(1)-O(6)	64.39(5)	O(12)-Eu(1)-O(13)	50.04(5)	N(7)-Eu(1)-H(1WA)	98.1
O(5)-Eu(1)-O(6)	47.52(4)	O(10)-Eu(1)-O(13)	66.21(5)	O(2W)-Eu(1)-N(7)	152.38(5)
O(12)-Eu(1)-O(6)	69.56(5)	O(1W)-Eu(1)-O(8)	115.96(5)	O(3W)-Eu(1)-N(7)	80.95(5)
O(10)-Eu(1)-O(6)	140.47(5)	O(2W)-Eu(1)-O(8)	133.31(5)	O(4W)-Eu(1)-N(7)	67.03(5)

## RESULTS AND DISCUSSION

**IR spectrum and molar conductance:** For the IR spectrum of compound **1**, there is a broad weak peak observed at near  $3443\text{ cm}^{-1}$ , which corresponds to the stretching vibrations of O-H of coordinated water molecules. The presence of broad band at  $3054\text{ cm}^{-1}$  indicating the hydrogen bonds between the N-H bonds and other atoms. The features at  $1503$ ,  $1305$ ,  $1035$ ,  $815$  and  $715\text{ cm}^{-1}$  may be assigned to the bidentate coordinated nitrate radical. While the strong peak at about  $1384\text{ cm}^{-1}$  is associated with the free nitrate radical. The free ligand 4,4'-bipyH in the compound shows characteristic absorption bands at  $1523$ ,  $1414$ ,  $1210$  and  $1078\text{ cm}^{-1}$ , which is well consistent with X-ray diffraction structural analysis.

The molar conductance of compound **1** was conducted at  $25\text{ }^{\circ}\text{C}$ , the observed molar conductance value in  $1.0 \times 10^{-3}\text{ mol L}^{-1}$  aqueous DMF solution is  $101.8\text{ S cm}^2\text{ mol}^{-1}$ , which indicating that the compound **1** is electrolyte, suggesting two nitrate anions show negative bivalent in outer sphere, while two protonated 4,4'-bipyridyl balancing the charge in outer sphere. This is consistent with the single-crystal X-ray analyses.

**Structural description:** The crystal structure of the compound is shown in Fig. 1 the asymmetric unit of the compound  $[\text{Eu}(\text{NO}_3)_3(\text{H}_2\text{O})_4] \cdot (4,4'\text{-bipyH})_2 \cdot (\text{NO}_3)_2$  consists of one Eu(III), five  $\text{NO}_3^-$ , two 4,4'-bipyH and four water. Eu(III) atom is coordinated with three  $\text{NO}_3^-$  and four water. The  $\text{NO}_3^-$  are bidentate so that the Eu atom is ten-coordinate (Fig. 2). Average bond lengths are: Eu-O (nitrate),  $0.25757\text{ nm}$ ; Eu-OH<sub>2</sub>,  $0.24216\text{ nm}$ , which are similar to the reported complexes  $[\text{Yb}(\text{NO}_3)_3(\text{H}_2\text{O})_4] \cdot 2(4\text{-bipyH})(\text{NO}_3)(\text{III})$  and  $[\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_4] \cdot 2(4\text{-bipyH})(\text{NO}_3)(\text{III})$ <sup>14</sup>. The coordination geometry can be described as follows. Compound present an distorted dicapped square antiprism geometry. Atoms O1W, O2W, O6 and O13 define a quadrangle and the other quadrangle of atoms O3W, O4W, O5, O10 are below the plane. Two cap atoms O12 and O8, respectively occupy the top and bottom of the square antiprism. The shorter H<sub>2</sub>O-N(bipy) distances and the near-collinearity of the H<sub>2</sub>O-N vectors with the 4,4'-bipyridyl N-N axes strongly imply the presence of hydrogen bonds (Table-3). The resulting three-dimensional net is reinforced by  $\text{NO}_3\text{-H}_2\text{O}$  bonds parallel to a axis, which is similar to the Ho compound<sup>15</sup>. The other two independent  $\text{NO}_3^-$  lies on a general position and two lie on crystal inversion centres, while the independent protonated 4,4'-bipyridyl molecules are on general positions.

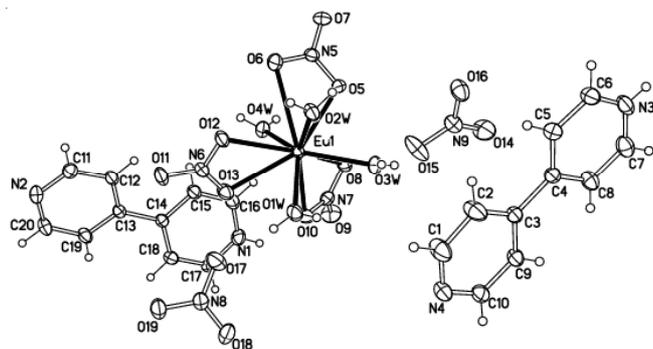


Fig. 1. Molecular structure of the title compound with thermal ellipsoids shown at the 30 % level

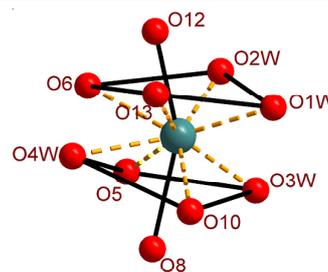


Fig. 2. Coordinate of the title compound

TABLE-3  
HYDROGEN BOND GEOMETRY FOR TITLE COMPLEX (nm,  $^{\circ}$ )

D-H...A	D-H	H...A	D...A	D-H...A
O(1W)-H(1WB)...O(17)	0.078	0.198	0.2746(2)	166.1
O(1W)-H(1WA)...O(7) <sup>i</sup>	0.074	0.219	0.2914(2)	166.0
O(2W)-H(2WB)...N(4) <sup>ii</sup>	0.083	0.196	0.2786(2)	173.1
O(2W)-H(2WA)...O(16) <sup>iii</sup>	0.083	0.201	0.2839(2)	177.3
O(3W)-H(3WB)...N(2) <sup>iv</sup>	0.079	0.199	0.2765(2)	169.0
O(3W)-H(3WA)...O(15)	0.075	0.220	0.2933(2)	163.9
O(4W)-H(4WB)...O(18) <sup>ii</sup>	0.079	0.190	0.2678(2)	167.0
O(4W)-H(4WA)...O(9) <sup>v</sup>	0.077	0.217	0.2892(2)	157.0
N(3)-H(80A)...O(16) <sup>vi</sup>	0.075	0.209	0.2811(3)	160.6
N(1)-H(81A)...O(7) <sup>v</sup>	0.079	0.217	0.2957(3)	173.3

Symmetry codes: <sup>i</sup>x-1,y,z; <sup>ii</sup>x+1,y,z; <sup>iii</sup>-x+1,-y+1,-z; <sup>iv</sup>x,y+1,z; <sup>v</sup>-x+2,-y+1,-z+1; <sup>vi</sup>-x+1,-y+2,-z.

In addition, there are infinite parallel aromatic rings from the 4,4'-bipyridyl, the 4,4'-bipyridyl cycles between two adjacent molecules are parallel with the centroid distance of  $0.36681\text{ nm}$ . Hence the hydrogen bonds and  $\pi$ - $\pi$  stacking interactions strengthen the stability of coordination compound (Fig. 3).

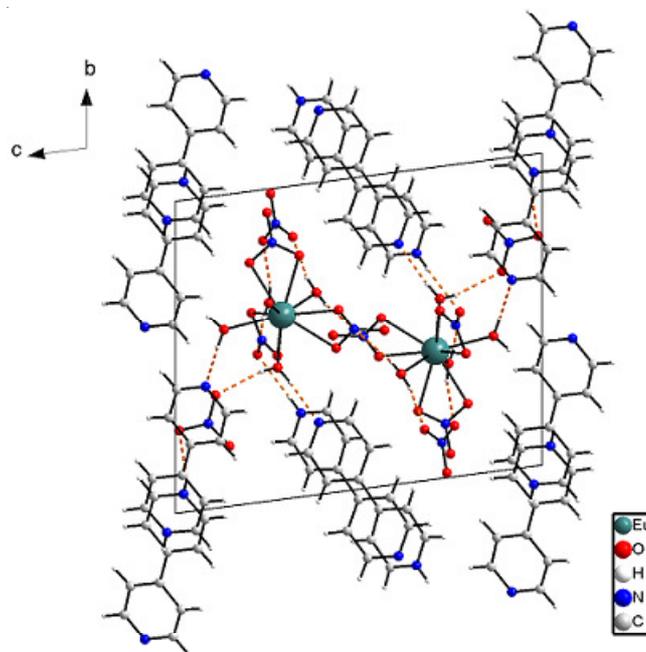


Fig. 3. Packing plot of the title compound

**Thermogravimetric analysis:** The thermogravimetric analyses of the compound was conducted under air atmosphere when they were heated to  $800\text{ }^{\circ}\text{C}$  with a  $10\text{ }^{\circ}\text{C min}^{-1}$  temperature ramp (Fig. 4). The TG diagram reveals two distinct weight

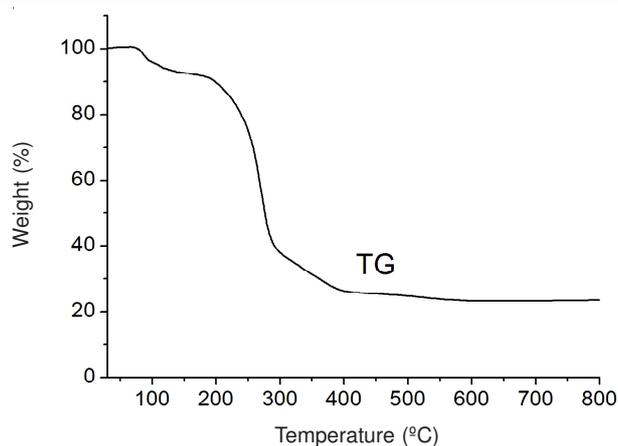


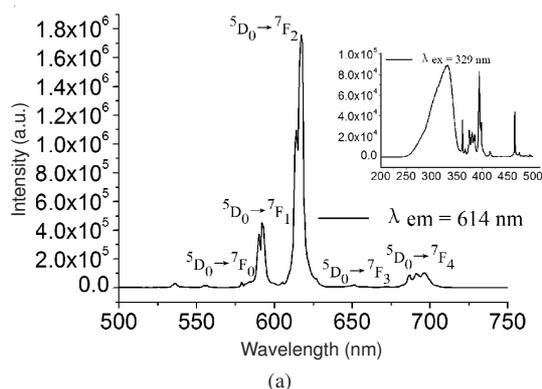
Fig. 4. TG of the title compound

regions. The first weight loss of 8.84 % (calcd. 8.49 %) corresponds to the release of four water molecule from 80-155 °C. The further decomposition occurred in the range of 200-420 °C with the weight loss of 70.23 % (calcd. 70.82 %), which is attributed to the elimination of five  $\text{NO}_3^-$  and two protonized 4,4'-bipyridyl. The residue weights 20.93 % corresponds to values calculated for  $\text{Eu}_2\text{O}_3$  20.74 %. This result is in good accordance with the composition of the compound.

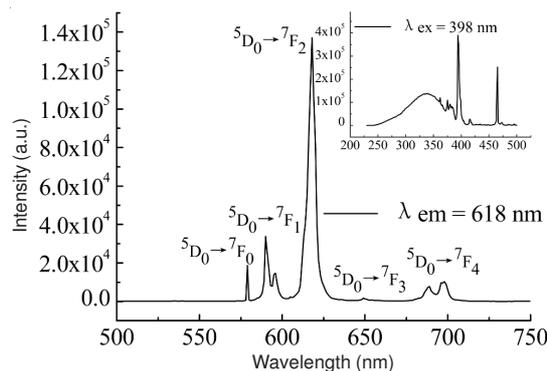
**Fluorescent property:** As shown in Fig. 5(a), intense red luminescence and exhibits characteristic peaks at 532, 590, 614, 647 and 695 nm can be observed, which are assigned to the  $4f \rightarrow 4f$  transitions of the  $^5\text{D}_0$  to  $^7\text{F}_j$  ( $J = 0, 1, 2, 3$  and  $4$ ) levels of Eu(III). It is well-known that for the Eu(III) ion, the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is hypersensitive to its site symmetry and of electric-dipole (ED) nature, which is only permitted on the condition when the Eu(III) ion occupies a site without an inversion center according to Judd-Ofelt theory<sup>16</sup>. By contrast, the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is insensitive to the site symmetry and of magnetic-dipole (MD) nature. The intensity ratio of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition reflects the information of the structures, such as ligand environments and site symmetry of Eu(III) ion. The intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is much stronger than that of  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition. These experimental facts suggest that the Eu(III) ion in compound **1** are not located at the symcenter, which is agree well with single-crystal X-ray analyses.

By comparing with the luminescence behaviour of pure free europium nitrate [Fig. 5(b)], it can be seen that the excitation is totally different, the feature excitation of the pure europium nitrate at 398 nm, while the title compound with the excitation at 329 nm identical to the excitation of the 4,4'-bipyridyl [Fig. 5(c)]. It is indicated that the emission for the title compound was enhanced may be due to 4,4'-bipyridyl can transfer the energy to the central metal efficiently and can sensitize the central metal.

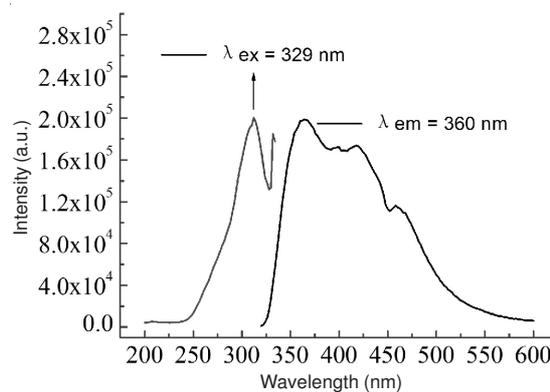
**Fluorescence quenching studies:** Fig. 6 shows that the emission spectra of EB bounded to DNA with compound. Upon addition of the tested compound, the emission intensity at 598 nm of EB-DNA system decreased in different degrees, indicating that the compound competes with EB to bind with DNA. The fluorescence quenching constant ( $K_{sq}$ ) of title compound is 1.82, the quenching plots illustrate that the quenching of EB-bound EB-DNA system by the title compound agree



(a)

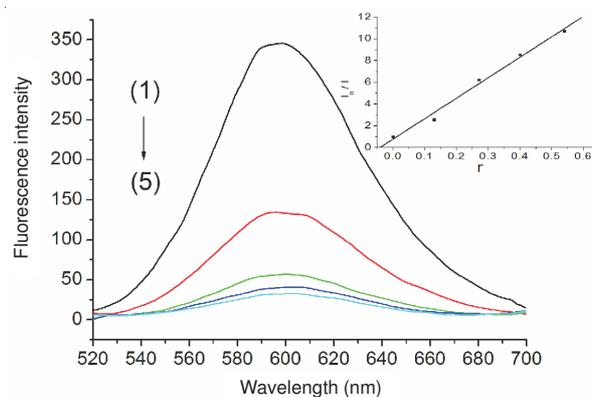


(b)



(c)

Fig. 5. Excitation and emission spectra in the solid state at room temperature: (a) the title compound (b) the pure europium nitrate (c) the 4,4'-bipyridyl

Fig. 6. Effects of the compound on the fluorescence spectra of EB-DNA system ( $r_1 = 0$ ;  $r_2 = 1.30$ ;  $r_3 = 2.70$ ;  $r_4 = 4.00$ ;  $r_5 = 5.40$ )

well with the Stern-Volmer equation<sup>17</sup>:  $I_0/I = 1 + K_{\text{sv}}I$ . It indicating that the compound could partially insert into the DNA double helix, because of the single cap four prism structures and the bipyridyl rings. These factors facilitate the compound to insert to the base of DNA molecule to compete with the combination of EB-DNA sites.

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